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Micellization and adsorption of zwitterionic surfactants at the air/water interface

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ABSTRACT

Zwitterionic surfactants are formally neutral but with headgroups containing both a positive charge center and a negative charge center separated from each other by a spacer group, with a long hydrophobic tail attached to one of the charge centers, usually but not always the positive charge center. The micellization and adsorption properties of zwitterionic surfactants depend on specifics of the surfactant structure such as the length ***m*** of the hydrophobic alkyl chain, the length ***n*** of the intercharge spacer and the nature of the headgroup charge centers. Micellization is favored by an increase in the hydrophobic tail length ***m***, but goes through a maximum for interchange spacings of ***n*** = 3–4 methylene groups. There are additional effects from the presence of additional hydrophilic substituent groups in the spacer. Specific binding of anions and the cation valence of added electrolyte are factors that also modulate the micellization and adsorption properties of zwitterionic surfactants in the presence of added electrolyte. Anions in particular bind preferentially to zwitterionic micelles independent of the relative order of the charge centers in the headgroup. The anion binding affinities follow a Hofmeister series and impart a net negative charge to the micelles. Micellization is temperature-dependent and exhibits enthalpy-entropy compensation, with entropy dominant at lower temperatures and enthalpy more important at higher temperatures. The judicious manipulation of these factors permits control of the interfacial properties of zwitterionic surfactants, responsible for a wide range of applications in chromatography, electrophoresis, cloud point extraction, solubilization, stabilization of biomolecules and nanomaterials and catalysis.

1. Introduction

Zwitterionic surfactants exhibit high water solubility, a wide isoelectric range, and high foam stability [1]. As a result, they have found applications in sensing, catalysis, and nanoparticle stabilization [2–4•,5–9]. Due to their excellent biodegradability, low toxicity, and skin and eye compatibility, zwitterionic surfactants are also of interest to the cosmetics and pharmaceutical industries [2]. Moreover, zwitterionic surfactants are widely employed as model systems for biological membranes, which contain a substantial proportion of zwitterionic phospholipid molecules [10,11].

The unique properties of zwitterionic surfactants stem from their structure. Typically, the structures of synthetic zwitterionic surfactants combine long hydrophobic alkane tails (represented here as $-(CH_2)_{m-1}CH_3$, where ***m*** is the number of carbons in the tail) with a polar headgroup consisting of positively and negatively charged groups in tandem The influence of the opposite charges in the surfactant headgroup can be tuned by varying the intercharge separation, usually by changing the length of an alkyl chain spacer (represented here as $-(CH_2)_n-$, where ***n*** is the number of methylene groups in the spacer chain) [12•,13]. The chemical structure of the polar headgroup directly affects the properties of the zwitterionic surfactant and hence its potential applications [14]. Table 1 shows the structures of the more common zwitterionic surfactants. The positively charged group is usually a quaternary ammonium or an imidazolium group. The most commonly employed negatively charged groups are carboxylate, sulfonate or sulfate and these are generally located at the distal extremity of the surfactant headgroup. When phosphate groups are employed as the negative charge of zwitterionic surfactants, they are sometimes located in the proximal position in the headgroup, as in phosphocholine [10]. The relatively low pK_as for ionization of these groups, which can be further influenced by the positive charge center in a manner dependent on the length ***n*** of the intervening spacer chain [15], contribute to the wide isoelectric range of zwitterionic detergents.

The net hydrophilicity/hydrophobicity of zwitterionic surfactants depends on the length of the hydrophobic tail, ***m*** [16], and on two opposing effects due to the intercharge spacer group: as ***n*** increases,

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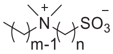
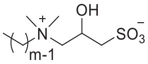
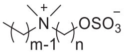
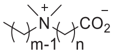
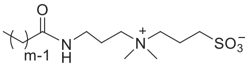
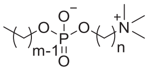
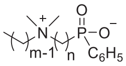
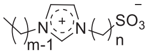
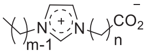
Table 1
Structures of the principal types of zwitterionic surfactants.

Surfactant type	Structure	Designation
Sulfobetaine		SBn-m
Hydroxypropyl sulfobetaine		HSB3-m
Sulfatobetaine		SaBn-m
Carboxybetaine or betaine		CBn-m
Amidosulfobetaine		ASB-m
Phosphocholine		PCn-m
Phenylphosphinatobetaines		PBn-m
Sulfo-imidazolium		ImSn-m
Carboxy-imidazolium		ImCn-m

the hydrophilicity of the spacer decreases whereas its dipole moment increases [13]. As a result, comparing the net hydrophobicity of surfactants with the same hydrophobic tail, zwitterionic surfactants are intermediate between ionic and nonionic surfactants [15].

2. Aqueous solubility and the Krafft temperatures of zwitterionic surfactants

Surfactant solubility depends on the nature of the alkyl chain and headgroup, as well as the presence of added salt. Betaine and phosphocholine surfactants are generally highly soluble in aqueous medium. The solubility of sulfobetaines decreases with increasing hydrocarbon chain length, and sulfobetaines are less soluble than carboxybetaines due to the lower hydrophilicity of sulfate relative to carboxylate groups [14–17•,18]. Replacing ammonium by imidazolium groups in betaine/sulfobetaine surfactants leads to a marked decrease in their room temperature solubility in aqueous media, presumably reflecting the increased surfactant headgroup rigidity and crystal packing conferred by the imidazolium moiety. As in the case of their ammonium counterparts, carboxy-imidazolium surfactants are more soluble than sulfo-imidazolium surfactants, and their solubility decreases with increasing hydrocarbon chain length. Addition of salt weakens intermolecular interactions and increases the solubility of carboxyl-imidazolium and sulfo-imidazolium surfactants in aqueous solution [18]. Section 6 discusses in more detail the important interactions between ions and zwitterionic surfactants.

The surfactant Krafft Temperature T_K is the temperature at which the solubility of the surfactant in aqueous medium becomes equal to its CMC. Below the T_K, monomeric surfactant is in equilibrium with the hydrated solid surfactant and micelles are absent. At the T_K, micelle formation begins, resulting in a dramatic increase in surfactant solubility above T_K. Not surprisingly, the T_K of zwitterionic surfactants depends critically on the nature of the headgroup. For homologous series, the values of T_K are lower for carboxybetaines compared to sulfobetaines [15], once again due to the greater hydrophilicity of the carboxylate group compared to sulfate. Moreover, for a given chain length, the T_K of imidazolium-containing zwitterionic surfactants is much higher than that of the ammonium counterparts [4•].

In general, T_K of zwitterionic surfactants varies with both ***m*** and ***n*** in a homologous series [15]. For example, sulfobetaines with a three carbon spacer group (SB3-m) show an increase in T_K with increasing surfactant tail length ***m*** due to the increase in the hydrophobic character of the molecule (Table S1). On the other hand, for the sulfobetaine series with a 16 carbon tail (SBn-16), upon increasing the spacer length ***n***, the value of T_K initially decreases, goes through a minimum at ***n*** = 3 or 4 and then increases at higher ***n***. This peculiar behavior is a result of the two opposing effects mentioned above, i.e., increasing hydrophobicity and increasing dipole moment of the spacer with increasing ***n***. While greater hydrophobicity favors a higher T_K, a larger dipole moment has the opposite effect. These results are consistent with the variation of the CMC values as a function of ***n*** (discussed in Section 3).

3. Length of the alkyl chain tail

The number of methylene groups $(-CH_2-)_{m-1}$ in the zwitterionic surfactant hydrophobic chain has a strong influence on its micellar and interfacial properties. For sulfobetaine, carboxybetaine, carboxy-imidazolium, and sulfo-imidazolium homologous series [15], the CMC values decrease with increasing ***m*** (Table S2) [4•,14–16,19], as expected given the well-known importance of the hydrophobic effect as a driving force for the micellization process [20]. As in the case of ionic and nonionic surfactants [21], the empirical Stauff-Klevens rule relating the logarithm of the CMC to the length of the hydrophobic chain also applies to zwitterionic surfactants, as shown in Eq. (1):

$$\log(CMC) = A + Bm \qquad (1)$$

In this equation, the coefficient *A* depends on charge, hydrophilic headgroup type, and added salt, as well as temperature; *B* measures the effect of each additional methylene group on the CMC, and is directly related to the free energy change, $\Delta_{tr}G/CH_2$, for transfer of a methylene group from the intermicellar aqueous medium to the micellar aggregate, viz., $B = (\Delta_{tr}G/CH_2)/2.303RT$, where *R* is the ideal gas constant.

For ionic surfactants, *B* values usually lie in the range of −0.25 to −0.35 [22], whereas for both nonionic and zwitterionic surfactants *B* is close to −0.5 (Table S3), meaning that for zwitterionic detergents the CMC decreases by a factor of 10 for every two additional methylene groups added to the hydrophobic chain. The higher value of *B* for zwitterionic surfactants relative to ionic surfactants reflects fundamental differences in electrostatic interactions at the micelle surface between ionic and zwitterionic headgroups that decrease the relative hydrophobic contribution of the hydrocarbon tails in the case of ionic micelles.

On the other hand, the *A* values, which are approximately 1.5 for ionic surfactants [16], are about twice as large for zwitterionic surfactants, again reflecting fundamental differences in electrostatic interactions. Typical *A* values are ca. 3.1 for sulfobetaine, carboxybetaine, and phosphocholine surfactants, and approximately 2.8 for carboxy-imidazolium and sulfo-imidazolium surfactants (Table S3) [4•,16]. The smaller values of *A* for imidazolium-containing surfactants, relative to their ammonium counterparts, are related to packing and intermolecular forces, as discussed above.

For homologous series of zwitterionic surfactants, the micellar aggregation number (N_{agg}) increases with increasing alkyl chain length of the tail (Table S2). This result is consistent with the decrease in CMC values with increasing ***m***, further highlighting the importance of the hydrophobic effect in micellization. Zwitterionic surfactants with longer hydrocarbon chains have greater capacity to decrease the surface tension of water [19,23] and the limiting value of the surface tension at the CMC (γ_{cmc}) decreases with increasing ***m (Table S4)***, reflecting the higher surface activity of surfactants with longer hydrophobic tails.

The hydrocarbon chain of the tail also affects the maximum Gibbs surface excess (Γ_{max}) and the area per molecule occupied by the polar headgroup [19,23]. Γ_{max} increases and A_{min} decreases with increasing alkyl chain length, since adsorbed molecules with longer chains tend to pack more densely at the air/water interface due to the increase in